On the thermodynamic behaviour of non-hyperelastic elastic materials

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ON THE BASIS of a recently proposed way of exploiting the second principle of thermodynamics, the behaviour of elastic dissipative materials is analysed. A mathematical model for these materials is considered in detail. It is shown how the functions representing internal energy and entropy can be experimentally determined once heating supply and stress during isothermal processes are measured. Conditions are given which, if met, assure that the limits of the elastic behaviour deduced on a thermodynamical basis can be actually reached by the material.

Przeanalizowano zachowanie się sprężystych materiałów dysypatywnych korzystając z niedawno zaproponowanego nowego sposobu wykorzystania drugiej zasady termodynamiki. Szczegółowo rozpatrzono model matematyczny omawianych materiałów. Przedstawiono sposób eksperymentalnego wyznaczania energii wewnętrznej i entropii na podstawie pomiarów przepływu ciepła i naprężeń występujących w procesie izotermicznym. Podano warunki, których spełnienie gwarantuje, że materiał rzeczywiście osiąga granice zachowania sprężystego określone w wyniku rozważań termodynamicznych.

Проанализировано поведение упругих диссипативных материалов, используя недавно предложенный новый способ использования второго начала термодинамики. Подробно рассмотрена математическая модель обсуждаемых материалов. Представлен экспериментальный способ определения внутренней энергии и энтропии на основе измерений течения тепла и напряжений, выступающих в изотермическом процессе. Приведены условия, удовлетворение которым гарантирует, что материал действительно достигает пределов упругого поведения, определенных в результате термодинамических рассуждений.

1. Introduction

MANY practical materials exhibit a springy or elastic behaviour in that they have a time-independent stress-strain response and, moreover, they recover their original stress-free configuration once the external loads are removed. In continuum mechanics, however, such properties are not usually considered as being the landmark of elastic behaviour. The latter is regarded as relevant to more particular classes of materials such as, for instance, *elastic materials*, *hyperelastic materials* and *thermoelastic materials*. The definitions of these materials are given in many textbooks and will not be reported here (cf., e.g. [6] for a clear and concise account). From these definitions it follows that for isothermal and for isentropic deformation processes every thermoelastic material behaves as an elastic one. If, moreover, the inequality expressing the second principle of thermodynamics is regarded as setting restrictions on the constitutive equations of the material, a well-known procedure [2] leads to the conclusion that every thermoelastic material must be hyperelastic for isothermal and for isentropic processes [3].

This procedure, however, is not the only viable nor the only physically possible one. Its validity, moreover, is not free from criticism [8, 12]. An alternative procedure is that

of exploiting the inequality expressing the second principle to find restrictions on the processes of a material, rather than on its constitutive equations [7, 11]. If such an approach is adopted, however, one cannot exclude that there are materials which, while behaving as elastic materials for isothermal or for isentropic processes, are not hyperelastic for the same processes. With these materials the present paper will be concerned.

By adopting the alternative thermodynamic procedure mentioned above, it has been shown in [11] that the range of processes where a material exhibits thermoelastic properties cannot, in general, be entirely described by one set of thermoelastic constitutive equations only. Different processes must be governed by different sets of thermoelastic constitutive equations if the material has to conform to the requirements imposed by the second principle of thermodynamics. The path-dependent character of the material response appears, therefore, as being a consequence — generally an unavoidable one — of a physical principle; not as featuring a particular choice of the constitutive equations.

Clearly, it is always possible to represent a path-dependent behaviour by means of a single set of history-dependent constitutive functions. However, if we adopt different sets of history-independent constitutive equations and exploit the second principle so as to determine which set holds in which process, we may obtain a simpler theoretical procedure. This is what has already been done in [9] and [11] and will be repeated in the present paper.

The analysis which follows is suitable for representing a more general notion of elasticity than the one usually considered in continuum mechanics. It applies to materials which possess a time-independent stress-strain response, recover their initial stress-free configuration once they are unloaded, and yet exhibit a dissipative behaviour. Dissipation arises both because the stress tensor does not derive from a potential (which may be due to the action of some sort of stress-dependent internal friction), and because the stress-strain response is process-dependent. It is worth emphasizing, actually, that the mere lack of a potential for the stress tensor does not entail by itself the fact that the stress-strain response should be path-dependent (cfr., e.g. the class of materials considered in [9]). On the other hand, a process-dependent stress-strain response does necessarily lead to the phenomenon known as *elastic hysteresis* [4, p. 138], which while recognized for a long time [5, 1] and affecting many elastic materials — notably rubber and steel — has hitherto been neglected in continuum mechanics.

In order to provide an easy theoretical model for dissipative materials enjoying thermoelastic properties, it was assumed in [11] that the behaviour of these materials could be described by two different sets of constitutive equations of the thermoelastic type. Each set of constitutive equations was relevant to a different class of deformation processes: loading deformation processes and unloading deformation processes, respectively. Because of this, some constitutive quantities such as stress tensor, specific internal energy and specific entropy were allowed to be discontinuous in the passage from one class of processes to the other. Even if it seems unlikely that these discontinuities do really exist, the proposed theory may be regarded as a simple and yet reasonable approximation of the real behaviour of elastic materials (cf. the comments of [11] discussing the experimental results of [1]). Moreover, at least for a certain kind of phenomena (e.g. vibration damping under isothermal conditions in the elastic range) the proposed model is certainly

better than the one in which the above discontinuities are ruled out simply by adopting the ordinary thermoelastic theory.

In the present paper our attention will be confined to a particular subclass of materials in which the stress tensor is represented by two different constitutive equations of the thermoelastic type. It will be proved in Sect. 3 that under appropriate conditions both specific internal energy and specific entropy must be represented by the same functions in either set of constitutive equations. From this result some properties of the stress tensor will be deduced in Sect. 5. In Sect. 6 it will be shown how internal energy and entropy can be determined experimentally from measurable quantities. Since the materials considered in this paper can undergo irreversible deformation processes only (if we exclude the trivially reversible ones represented by rigid-body motions), the results of Sect. 6 should confute the statement sometimes claimed that entropy is a quantity which cannot be determined experimentally for states of deformation which can be reached through irreversible processes only.

Dealing with the same kind of materials as the ones considered here, it was shown in [11] that there may be limit states of deformation beyond which no deformation process can be compatible with the laws of thermodynamics unless changes in the behaviour of the material occur. It was not excluded, however, that a material could leave off obeying the original constitutive equations before the above limit states were attained. In Sect. 7 a class of materials exhibiting thermoelastic properties will be defined for which one can establish conditions assuring that the above limit states must actually be reached by the material before it could leave off obeying its original constitutive equations. These conditions do not seem too restrictive and appear to be in good agreement with the behaviour of many practical materials. When they are met, the limit to the elastic behaviour of a material can be predicted by thermodynamic arguments based on the constitutive equations of the material in the elastic range.

2. Definition of thermoelastic material with hysteresis and summary of basic notation

In what follows we shall keep as far as possible the same notation adopted in [11]. We shall make explicit reference to that paper when dealing with quantities or definitions not previously set forth in the present article. We shall indicate by X, θ and t material coordinates, temperature and time, and by x, ϱ, T, b, ε, q, r and η the spatial coordinates of the particle represented by X, the mass density in the actual configuration, the Cauchy stress tensor, the external body force, the specific internal energy, the heating flux vector referred to the actual configuration, the heating supply and the specific entropy. Since we shall have to refer to two distinct sets of constitutive relations, we shall distinguish the quantities relevant to one or the other of these sets by appending to them the symbol ''or' respectively. For easy reference we shall record here the expression of the *stress working w*:

$$(2.1) \qquad w = \mathrm{tr}(T\dot{F}F^{-1}), \qquad (F = \partial x/\partial X),$$

the local form of the law of balance of momentum:

$$(2.2) \qquad \varrho\ddot{x} - \mathrm{div}\,T = \varrho b,$$

the local form of the first principle of thermodynamics:

$$(2.3) \qquad\qquad \varrho\dot{\varepsilon} - w + \mathrm{div}\,\mathbf{q} = \varrho r$$

and the reduced local form of the Clausius-Planck inequality here assumed as the second principle of thermodynamics [10]:

$$(2.4) \qquad\qquad -\varrho(\partial_\theta\hat{\psi} + \eta)\dot{\theta} + \mathrm{tr}\{[\mathbf{F}^{-1}\mathbf{T} - \varrho(\partial_\mathbf{F}\hat{\psi})^T]\dot{\mathbf{F}}\} \geqslant 0,$$

where the function $\psi = \hat{\psi}(\mathbf{F}, \theta)$ defined by

$$(2.5) \qquad\qquad \psi = \varepsilon - \theta\eta$$

is the specific free energy expressed taking $\mathbf{F}$ and θ as independent variables.

By introducing the second order tensor $\mathbf{B}$ defined by

$$(2.6) \qquad\qquad \mathbf{B} = (\mathbf{F}^{-1}\mathbf{T})^T - \varrho\partial_\mathbf{F}\hat{\psi},$$

we can write Eq. (2.4) in the form

$$(2.7) \qquad\qquad -\varrho(\partial_\theta\hat{\psi} + \eta)\dot{\theta} + \mathrm{tr}(\mathbf{B}^T\dot{\mathbf{F}}) \geqslant 0,$$

which for isothermal processes reads

$$(2.8) \qquad\qquad \mathrm{tr}(\mathbf{B}^T\dot{\mathbf{F}}) \geqslant 0.$$

We shall indicate by s the amount of total specific heating and we shall attribute to s a positive sign when it represents a quantity of heat which is absorbed by the body. It is clear that

$$(2.9) \qquad\qquad \int_\mathscr{B} s\,dm = \int_\mathscr{B} r\,dm - \int_{\partial\mathscr{B}} \mathbf{q}\cdot\mathbf{n}\,dA,$$

where $\mathscr{B}$ indicates the region occupied by the body, $\partial\mathscr{B}$ its surface, dA an element of this surface and $\mathbf{n}$ its outward unit normal. By expressing Eq. (2.9) in local form we get

$$(2.10) \qquad\qquad s = \varrho r - \mathrm{div}\,\mathbf{q}.$$

It has been shown in paper [11] that the behaviour of a thermoelastic material which is not hyperelastic for isothermal or isentropic processes cannot be described in a consistent way by means of a single set of constitutive equations which express $\mathbf{T}$, ε, η and $\mathbf{q}$ as single-valued functions of the actual values of $\mathbf{F}$, θ and $\mathbf{g} = \mathrm{grad}\,\theta$. In the same paper a proposal has been made to describe such a material by means of two distinct sets of single-valued constitutive equations, namely:

$$(2.11) \qquad\qquad \mathbf{T}' = \hat{\mathbf{T}}'(\mathbf{F}, \theta),$$

$$(2.12) \qquad\qquad \varepsilon' = \hat{\varepsilon}'(\mathbf{F}, \theta),$$

$$(2.13) \qquad\qquad \eta' = \hat{\eta}'(\mathbf{F}, \theta),$$

$$(2.14) \qquad\qquad \mathbf{q}' = \hat{\mathbf{q}}'(\hat{\mathbf{q}}\mathbf{F}, \theta, \mathbf{g}),$$

and

$$(2.15) \qquad\qquad \mathbf{T}'' = \hat{\mathbf{T}}''(\mathbf{F}, \theta),$$

$$(2.16) \qquad\qquad \varepsilon'' = \hat{\varepsilon}''(\mathbf{F}, \theta),$$

$$(2.17) \qquad\qquad \eta'' = \hat{\eta}''(\mathbf{F}, \theta),$$

$$(2.18) \qquad\qquad \mathbf{q}'' = \hat{\mathbf{q}}''(\mathbf{F}, \theta, \mathbf{g}).$$

Moreover, an appropriate criterion to distinguish the processes in which the response of the material is represented by Eqs. (2.11)–(2.14) from those in which the response of the material is represented by Eqs. (2.15)–(2.18), has been given.

Since, however, the constitutive equations (2.11)–(2.18) can represent a material which does not exhibit any feature of what is commonly thought of elastic behaviour, we shall specify further the class of materials we are considering, by means of the following

DEFINITION 2.1. *We shall define a thermoelastic material with hysteresis as a material having the following properties*:

(i) *For every state of uniform temperature θ there exists and is unique (to within of rigid-body motions) a stress-free state of deformation* (natural state at the given temperature).

(ii) *If during a process the stress working w is greater than zero, then stress tensor, internal energy, entropy and heating flux are uniquely determined by* $\mathbf{F}$, θ *and* $\mathbf{g}$ *through the relations* (2.11)–(2.14). *If, however, during a process w < 0, the above quantities are uniquely determined by the values of* $\mathbf{F}$, θ *and* $\mathbf{g}$ *through the relations* (2.15)–(2.18).

(iii) *If during a process w = 0, then* $\mathbf{T}$, ε, η *and* $\mathbf{q}$ *are not, in general, uniquely determined by* $\mathbf{F}$, θ *and* $\mathbf{g}$, *but their values (or the values of their components if they are vectors or tensors) must be contained between the values which the corresponding quantities* (2.11)–(2.14) *and* (2.15)–(2.18) *assume in correspondence to the same state of deformation and temperature.*

(iv) *If the stress working for a deformation increment* $\dot{\mathbf{F}}\, dt$ *is greater than zero, then the stress working for the deformation increment* $-\dot{\mathbf{F}}\, dt$ *is less than zero.*

Observe that the condition iv of the previous definition is not a truism. Indeed, it is not trivially met when $\mathbf{T}' \neq \mathbf{T}''$. This condition has to be introduced if, according to what is commonly thought about elastic behaviour, we want the material to recover spontaneously (i.e. without absorbing work from the external forces) the state assumed before the application of the external forces, once the latter have been slowly removed. In this paper we shall be concerned mainly with isothermal processes. We shall, therefore, admit that the reference configuration ($\mathbf{F} \equiv \mathbf{1}$) coincides with the natural state of the body at the considered temperature θ. We shall indicate by $\{\mathbf{F}\}_{0,\theta}$ the set of deformation gradients which can be obtained from $\mathbf{F} \equiv \mathbf{1}$ by means of rigid-body motions at constant temperature θ.

When $w = 0$, Definition 2.1 item iii tells us that the quantities $\mathbf{T}$, ε, η and $\mathbf{q}$ are not, in general, uniquely determined by $\mathbf{F}$, θ and $\mathbf{g}$. It turns out that in the present model $\mathbf{T}$, ε, η and $\mathbf{q}$ are generally discontinuous in the passage from a process in which a set of constitutive equations holds to a process in which the other set of constitutive equations holds. We shall assume, henceforth, that $\hat{\mathbf{T}}'$ and $\hat{\mathbf{T}}''$ do not coincide ([1]) and we shall prove in the next section that under appropriate circumstances $\hat{\varepsilon}' \equiv \hat{\varepsilon}''$ and $\hat{\eta}' \equiv \hat{\eta}''$. Internal energy, entropy and free energy can, therefore, be represented by the single-valued functions $\varepsilon = \hat{\varepsilon}(\mathbf{F}, \theta)$, $\eta = \hat{\eta}(\mathbf{F}, \theta)$ and $\psi = \hat{\psi}(\mathbf{F}, \theta)$ for every process. The question whether $\hat{\mathbf{q}}'$ coincides with $\hat{\mathbf{q}}''$ or not, is irrelevant for the analysis which follows and will not be considered here.

We shall call a *loading deformation increment* an increment of deformation for which $w > 0$ and an *unloading deformation increment* an increment of deformation for which $w < 0$. For the sake of simplicity attention will be confined to the case of materials in

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([1]) As far as the experimental basis for the admissibility of this hypothesis cf. [11, p. 238].

which $\mathbf{T}'$ and $\mathbf{T}''$ have the same principal axes, no matter what the values of $\mathbf{F}$ and θ are. This means that

$$(2.19) \qquad\qquad \hat{\mathbf{T}}' = \hat{a}(\mathrm{I}, \mathrm{II}, \mathrm{III}, \theta)\hat{\mathbf{T}}'',$$

where $a = \hat{a}(\mathrm{I}, \mathrm{II}, \mathrm{III}, \theta)$ is a scalar function of the strain invariants I, II, III and of θ. We shall assume, moreover, that also the tensor $\mathbf{F}(\partial_{\mathbf{F}}\hat{\psi})^T$ has the same principal axes as $\mathbf{T}'$ and $\mathbf{T}''$; that is

$$(2.20) \qquad\qquad \varrho\mathbf{F}(\partial_{\mathbf{F}}\hat{\psi})^T = \hat{b}(\mathrm{I}, \mathrm{II}, \mathrm{III}, \theta)\hat{\mathbf{T}}',$$

werhe $b = \hat{b}(\mathrm{I}, \mathrm{II}, \mathrm{III}, \theta)$ is another scalar function. Clearly, from Eqs. (2.19) and (2.20) it follows that

$$(2.21) \qquad\qquad \varrho\mathbf{F}(\partial_{\mathbf{F}}\hat{\varphi})^T = \hat{c}(\mathrm{I}, \mathrm{II}, \mathrm{III}, \theta)\hat{\mathbf{T}}'',$$

where

$$(2.22) \qquad\qquad \hat{c}(\mathrm{I}, \mathrm{II}, \mathrm{III}, \theta) = \hat{a}(\mathrm{I}, \mathrm{II}, \mathrm{III}, \theta)\hat{b}(\mathrm{I}, \mathrm{II}, \mathrm{III}, \theta).$$

It will be shown in Sect. 5 that $\hat{a}(\mathrm{I}, \mathrm{II}, \mathrm{III}, \theta) \geqslant 1$, that $\hat{c}(\mathrm{I}, \mathrm{II}, \mathrm{III}, \theta) \geqslant 1$ and that $0 < \hat{b}(\mathrm{I}, \mathrm{II}, \mathrm{III}, \theta) \leqslant 1$. Under these circumstances it is an easy task to verify that when $b \neq 1$ and $c \neq 1$ the above definitions of loading and unloading deformation increments are completely equivalent to the more general ones given in [11, § 4]. However, when $b = 1$ or $c = 1$, a loading deformation increment or an unloading one, according to the previous definitions, turns out to be a *neutral* deformation increment as defined in [11, § 4]. As a consequence of this, when applying the Clausius-Planck inequality to a loading or to an unloading deformation increment, we shall be unable to exclude at the outset the equality sign from that relation.

3. A condition implying $\hat{\varepsilon}' \equiv \hat{\varepsilon}''$ and $\hat{\eta}' \equiv \hat{\eta}''$. Relation between entropy and free energy

We know from experience that there are states of deformation and temperature in which a material can absorb or lose an amount of heat at constant values of $\mathbf{F}$ and θ. In these situations the material suffers changes in its molecular structure so that the amount of heat absorbed or lost balances the variation of internal energy due to the atomic rearrangement. This is, for instance, what happens when a crystalline solid undergoes a transition from an allotropic state to another, or when, more generally, thermal actions produce changes in the state of aggregation of a body. In these cases, an observer who describes the state of the body by means of the macroscopical variables $\mathbf{F}$ and θ sees that it absorbs or loses heat without corresponding changes in its deformation and temperature. Without attempting to go into the details of this question, but only to exclude such a kind of phenomena from the range of processes which the materials we are considering can undergo, we shall lay down the following:

DEFINITION 3.1. *We shall say that at time t a material undergoes a change in its state of aggregation if $s(t) \neq 0$ while $\dot{\mathbf{F}}(t) = 0$ and $\dot{\theta}(t) = 0$.*

The following proposition follows staightforwardly from the above definition:

PROPOSITION 3.1. *If in a thermoelastic material with hysteresis* $\mathbf{F}$ *and* θ *are kept constant and if, moreover, the material does not undergo changes in its state of aggregation, then the total specific heating* s *vanishes identically.*

On the basis of the forthcoming analysis the following theorems can now be proved.

THEOREM 3.1. *If at any time* t *the relations* $\dot{\mathbf{F}}(t) = \mathbf{0}$ *and* $\dot{\theta}(t) = 0$ *imply* $s(t) = 0$ *(that is if the material does not undergo changes in its state of aggregation), then* $\hat{\varepsilon}' \equiv \hat{\varepsilon}''$.

P r o o f. At a given state of deformation $_0\mathbf{F}$ and at a given temperature θ_0, consider a body element undergoing an isothermal loading-unloading transition and apply the first principle of thermodynamics to this process. If ε and $\mathbf{T}$ are the values assumed by the internal energy and the stress tensor during this process([2]), we have

$$(3.1) \qquad \int_{\Delta t} \dot{\varepsilon}\, dt = \int_{\Delta t} \mathrm{tr}(\mathbf{T}\dot{\mathbf{F}}\mathbf{F}^{-1})\, dt + \int_{\Delta t} s\, dt,$$

where Δt indicates the time interval in which the process takes place. Since we are considering a transition process, $\mathbf{F} = {_0\mathbf{F}} = \mathrm{const}$ and, therefore, $\dot{\mathbf{F}} \equiv \mathbf{0}$; moreover, since this process is an isothermal one, we have from Proposition 3.1 that $s = 0$. Thus,

$$(3.2) \qquad \int_{\Delta t} \dot{\varepsilon}\, dt = \hat{\varepsilon}''(_0\mathbf{F}, \theta_0) - \hat{\varepsilon}'(_0\mathbf{F}, \theta_0) = 0.$$

Hence, since $_0\mathbf{F}$ and θ_0 are arbitrary, we get

$$(3.3) \qquad \hat{\varepsilon}'(\mathbf{F}, \theta) \equiv \hat{\varepsilon}''(\mathbf{F}, \theta).$$

THEOREM 3.2. *If at any time* t *the relations* $\dot{\mathbf{F}}(t) = \mathbf{0}$ *and* $\dot{\theta}(t) = 0$ *imply* $s(t) = 0$, *then* $\hat{\eta}' \equiv \hat{\eta}''$.

P r o o f. By applying the second principle of thermodynamics to the same process considered in the previous theorem, we get

$$(3.4) \qquad \int_{\Delta t} \theta_0 \dot{\eta}\, dt \geqslant \int_{\Delta t} s\, dt,$$

where η indicates the values assumed by entropy ([3]) in the interval Δt. From Eq. (3.4) and from Proposition 3.1, we obtain

$$(3.5) \qquad \int_{\Delta t} \theta_0 \dot{\eta}\, dt \geqslant 0.$$

Hence, since $\theta_0 \geqslant 0$,

$$(3.6) \qquad \hat{\eta}''(_0\mathbf{F}, \theta_0) - \hat{\eta}'(_0\mathbf{F}, \theta_0) \geqslant 0.$$

([2]) As follows from Definition 2.1 item iii, during a transition process $\mathbf{T}$, ε and η can vary between the values defined by Eqs. (2.11)–(2.16) and Eqs. (2.15)–(2.17) for the considered values of $_0\mathbf{F}$ and θ_0. It is assumed that the transition process considered here takes place in a continuous way from the loading process from which it starts, to the unloading process at which it ends. Moreover, the quantities $\mathbf{T}$, ε and η are supposed to vary in a continuous way between the values $\mathbf{T}'$, ε', η' and $\mathbf{T}''$, ε'', η'', respectively. These assumptions seem reasonable from the physical standpoint and do not introduce serious limitations to the theory.

([3]) See footnote ([2]).

In a similar way, by considering an unloading-loading transition process inverse to the previous one, we get

(3.7) $\hat{\eta}'(_0F, \theta_0) - \hat{\eta}''(_0F, \theta_0) \geqslant 0.$

Thus, since $_0F$ and θ_0 are arbitrary, from (3.6) and (3.7) we get

(3.8) $\hat{\eta}'(F, \theta) \equiv \hat{\eta}''(F, \theta).$

We shall henceforth use the notation $\varepsilon = \hat{\varepsilon}(F, \theta)$ and $\eta = \hat{\eta}(F, \theta)$ for the functions (3.3) and (3.8), respectively. From Theorem 3.1 and Theorem 3.2 we can deduce:

COROLLARY 3.1. A thermoelastic material with hysteresis that does not undergo changes in its state of aggregation possesses a unique Helmholtz free energy function given by

(3.9) $\hat{\psi}(F, \theta) = \hat{\varepsilon}(F, \theta) - \theta\hat{\eta}(F, \theta);$

and

COROLLARY 3.2. If a thermoelastic material with hysteresis does not undergo changes in its state of aggregation, then $r = 0$ during homothermal loading-unloading (or unloading-loading) transitions.

The first of these corollaries is a consequence of Theorem 3.1 and Theorem 3.2. The second is a consequence of Proposition 3.1, of the definition of transition process and of the fact that on the mere basis of central symmetry properties ([4]) (that is without using thermodynamical arguments) it can be deduced that for homothermal processes $q = 0$; see [2, p. 173] and the work of Pipkin and Rivlin quoted there.

If the hypothesis is made that for any given values of F and θ the quantity θ can assume positive or negative values while $\dot{F} = 0$, then by applying the Clausius-Planck inequality and by repeating the same procedure as that proposed by COLEMAN and NOLL (cf. [3, p. 1122]) one can deduce that:

THEOREM 3.3. *If at any t the relations $\dot{F}(t) = 0$ and $\dot{\theta}(t) = 0$ imply $s(t) = 0$, then specific entropy and specific free energy are connected by the relation*

(3.10) $\hat{\eta}(F, \theta) = -\partial_\theta \hat{\psi}(F, \theta).$

It should be observed, however, that Eq. (3.10) is a consequence of the hypothesis that $\dot{\theta}$ can be greater or less than zero when $\dot{F} = 0$ and F and θ are arbitrary; not a necessary consequence of the second principle of thermodynamics (cf. the criticism expressed in [12]).

4. The structure of thermodynamically admissible processes

Unless otherwise specified, we shall from now on consider isothermal processes and we shall exclude the occurrence of phase changes. As shown in [11], the tensors B' and B'', defined according to Eq. (2.6) by

(4.1) $B' = B'(F, \theta) = (F^{-1}\hat{T}')^T - \varrho\partial_F\hat{\psi}$

([4]) Henceforth admitted.

and by

(4.2) $$\mathbf{B}'' = \hat{\mathbf{B}}''(\mathbf{F}, \theta) = (\mathbf{F}^{-1}\hat{\mathbf{T}}'')^T - \varrho\partial_{\mathbf{F}}\hat{\psi},$$

play a fundamental role as far as the determination of the thermodynamically admissible processes of a material are concerned. In this section we shall clarify the way in which a thermodynamically admissible process depends on $\mathbf{B}'$ and $\mathbf{B}''$. To begin with, we shall prove

THEOREM 4.1. *If* $\mathbf{B}' \neq 0$ *and if an irreversible* [5] *increment of deformation* $\dot{\mathbf{F}}dt$ *is thermodynamically compatible when the constitutive equations* (2.11)–(2.14) *hold, then its opposite* $-\dot{\mathbf{F}}dt$ *is not compatible with the same constitutive equations. Reciprocally, if an increment of deformation is not compatible when Eqs.* (2.11)–(2.14) *hold, then its opposite is* [6].

P r o o f. The condition of thermodynamical compatibility for an isothermal process is given by

(4.3) $$\mathrm{tr}(\mathbf{B}'^T\dot{\mathbf{F}}) \geqslant 0.$$

Since this inequality is a linear relation in $\dot{\mathbf{F}}$ and since the equality sign in Eq. (4.3) is excluded by the irreversibility hypothesis, the theorem follows straightforwardly.

Consider now a deformation increment $\dot{\mathbf{F}}dt$ such that all the components of $\dot{\mathbf{F}}\mathbf{F}^{-1}$ but one are equal to zero. The previous theorem tells us that either this deformation increment or its opposite is thermodynamically compatible when the constitutive equations (2.11)–(2.14) hold. Hence:

COROLLARY 4.1. If $\mathbf{B}' \neq 0$, there exists always a deformation increment which is both thermodynamically compatible when the constitutive equations (2.11)–(2.14) hold and such as all the components of $\dot{\mathbf{F}}\mathbf{F}^{-1}$ but one vanish in the given reference system[7].

The following theorem gives us details on $\mathbf{B}'$ and $\mathbf{B}''$:

THEOREM 4.2. *If a thermoelastic material represented by* (2.11)–(2.18) *is in a state of deformation in which* $\mathbf{B}' \neq 0$ *and* $\mathbf{B}'' \neq 0$, *and if starting from this state the material can suffer deformation increments in every direction, then* $\mathbf{B}'$ *and* $\mathbf{B}''$ *must be opposite tensors*[8].

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[5] An isothermal increment of deformation is said to be irreversible when the equality sign in Eq. (2.8) does not hold. Cf. [11, § 4].

[6] An analogous theorem holds true, of course, if we consider $\mathbf{B}''$ instead of $\mathbf{B}'$ and the constitutive equations (2.15)–(2.18) instead of Eqs. (2.11)–(2.14).

[7] Since $\mathrm{tr}(\mathbf{HK}) = H_{ij}K^{ji} = H^{ij}K_{ji} = H_i{}^jK_j{}^i$, it should be clear that this corollary applies either if reference is made to the covariant components of $\dot{\mathbf{F}}\mathbf{F}^{-1}$, or to the contravariant ones, or finally to the mixed ones.

[8] By direction of a second order tensor $\mathbf{S}$ we mean the angle

$$\varphi = \mathrm{arc}\cos\frac{\mathrm{tr}(\mathbf{S}^T\mathbf{R})}{|\mathbf{S}|\,|\mathbf{R}|}$$

which $\mathbf{S}$ forms with a given reference tensor $\mathbf{R}$ in the nine-dimensional space of the second rank tensors. Two tensors $\mathbf{S}$ and $\mathbf{Q}$ are said to be of the same direction or opposite if the relation

$$\mathbf{S} = \pm k^2\mathbf{Q}$$

holds with positive or negative sign, respectively, k being a real number. Cf. [11, § 2].

P r o o f. Let $\dot{\mathbf{F}}$ represent a loading deformation increment. The angle between $\mathbf{B}'$ and $\dot{\mathbf{F}}$ is given by

$$(4.4) \qquad\qquad \varphi' = \arccos \frac{\mathrm{tr}(\mathbf{B}'^T\dot{\mathbf{F}})}{|\mathbf{B}'||\dot{\mathbf{F}}|},$$

and from the second principle (2.8) we can deduce that $-\dfrac{\pi}{2} \leqslant \varphi' \leqslant \dfrac{\pi}{2}$. On the other hand, in view of Theorem 4.1, the deformation increment represented by $-\dot{\mathbf{F}}$ is not, in general, thermodynamically compatible when Eqs. (2.11)–(2.14) hold. Since by hypothesis $-\dot{\mathbf{F}}dt$ must be a deformation increment which the body can suffer, it follows that this deformation increment must be thermodynamically compatible when Eqs. (2.15)–(2.18) hold. Therefore the angle

$$(4.5) \qquad\qquad \varphi'' = \arccos \frac{\mathrm{tr}(-\mathbf{B}''^T\dot{\mathbf{F}})}{|\mathbf{B}''||\dot{\mathbf{F}}|}$$

has to be greater than $-\dfrac{\pi}{2}$ and less than $\dfrac{\pi}{2}$. Thus, both $\mathbf{B}'$ and $-\mathbf{B}''$ must be concordant[9] with $\dot{\mathbf{F}}$. Since $\dot{\mathbf{F}}$ can be any arbitrary tensor $\Big($provided that it forms an angle $-\dfrac{\pi}{2} \leqslant$ $\leqslant \varphi \leqslant \dfrac{\pi}{2}$ with $\mathbf{B}'\Big)$, it follows that $\mathbf{B}'$ and $-\mathbf{B}''$ must have the same direction. Thus

$$(4.6) \qquad\qquad \mathbf{B}' = -k^2\mathbf{B}''.$$

From the previous theorem it follows:

COROLLARY 4.2. Under the hypothesis Theorem of 4.2, the set of loading deformation increnents and that of unloading deformation increments constitute a set of pairwise opposite tensors.

5. Restrictions on $\hat{\mathbf{T}}'$ and $\hat{\mathbf{T}}''$

In this section we shall establish some properties which the functions $\hat{\mathbf{T}}'(\mathbf{F}, \theta)$ and $\hat{\mathbf{T}}''(\mathbf{F}, \theta)$ have to satisfy in order that the material they represent exhibits the behaviour set forth by Definition 2.1. We shall start with

THEOREM 5.1. *If $\theta = const$, both $\hat{\mathbf{T}}'$ and $\hat{\mathbf{T}}''$ must vanish when and only when $\mathbf{F} \in \{\mathbf{F}\}_{0,\theta}$. Moreover, for a given value of $\mathbf{F} \notin \{\mathbf{F}\}_{0,\theta}$, T'_{ij} and $T''_{ij}(i, j \in \{1, 2, 3\})$ must have the same sign.*

P r o o f. The first part of the theorem is a consequence of Definition 2.1 point i. To prove the second part consider an element of the body in a generic state of deformation $\mathbf{F}$ and consider the expressions of w when the element undergoes a loading deform-

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[9] Two tensors are said to be concordant when their angle is less than $\dfrac{\pi}{2}$ and greater than $-\dfrac{\pi}{2}$. Cf. [11, §2].

ation increment $_l\dot{\mathbf{F}}dt$ and an unloading deformation increment $_u\dot{\mathbf{F}}dt$, respectively. In view of Definition 2.1 point iii, we have

(5.1) $$w_l = \mathrm{tr}(\mathbf{T}'_l\dot{\mathbf{F}}\mathbf{F}^{-1}) > 0$$

and

(5.2) $$w_u = \mathrm{tr}(\mathbf{T}''_u\dot{\mathbf{F}}\mathbf{F}^{-1}) < 0.$$

As observed in Corollary 4.1, we can always choose $_l\dot{\mathbf{F}}$ as a tensor such that all contravariant components of $_l\dot{\mathbf{F}}\mathbf{F}^{-1}$ vanish, except one, say $(_l\dot{\mathbf{F}}\mathbf{F}^{-1})^{ij}$ which is equal to a real number k. Moreover, since the deformation increment represented by a tensor $_u\dot{\mathbf{F}}$ whose components are opposite to that of $_l\dot{\mathbf{F}}$ is an unloading deformation increment as stated by Corollary 4.2, it turns out that with such a choice of $_l\dot{\mathbf{F}}$ and $_u\dot{\mathbf{F}}$ the relations (5.1) and (5.2) become

(5.3) $$T'_{ij}k > 0$$

and

(5.4) $$-T''_{ij}k < 0.$$

Hence,

(5.5) $$T'_{ij}T''_{ij} > 0 \quad \text{(no sum)}.$$

We shall lay down the following:

DEFINITION 5.1. *We shall call internal stress the second order tensor defined by*

(5.6) $$\mathbf{T}^* = \hat{\mathbf{T}}^*(\mathbf{F}, \theta) = \varrho\mathbf{F}(\partial_{\mathbf{F}}\hat{\psi})^T.$$

From Corollary 3.1 we have that $\mathbf{T}^*$ is uniquely determined when $\mathbf{F}$ and θ are given. We can prove now

THEOREM 5.2. *If $\hat{\mathbf{T}}'$ and $\hat{\mathbf{T}}''$ are continuous and single valued functions of $\mathbf{F}$ and θ, then for an isothermal process we have*

(5.7) $$|\hat{T}'_{ij}| \geqslant |\hat{T}^*_{ij}| \geqslant |\hat{T}''_{ij}|.$$

Moreover, in correspondence to each value of $\mathbf{F}$ the components T'_{ij}, T''_{ij} and T^*_{ij} must all have the same sign.

P r o o f. Consider a body element in a state of deformation $\mathbf{F}$ and consider an increment of deformation $\dot{\mathbf{F}}^*dt$ such that the tensor $\dot{\mathbf{F}}^*\mathbf{F}^{-1}$ has all its contravariant components equal to zero except one, say $(\dot{\mathbf{F}}^*\mathbf{F}^{-1})^{ij}$ which has a positive value. We know from Theorem 5.1 that the homologous components of $\mathbf{T}'$ and $\mathbf{T}''$ must be of the same sign. Suppose that both T'_{ij} and T''_{ij} are positive. It follows from Definition 2.1 point ii that $\dot{\mathbf{F}}^*$ represents a loading deformation increment. Consider, then, an infinitesimal cycle of deformation which takes the element from $\mathbf{F}$ to $\mathbf{F}+\dot{\mathbf{F}}^*dt$ and again to $\mathbf{F}$. In the second part of this cycle the increment of deformation is represented by $-\dot{\mathbf{F}}^*$ and, as stated by Corollary 4.2, is an unloading deformation increment. By applying the second principle of thermodynamics to the two parts of the cycle we obtain

(5.8) $$\mathrm{tr}(\mathbf{B}'^T\dot{\mathbf{F}}^*) \geqslant 0$$

and

(5.9) $$\mathrm{tr}(-\mathbf{B}''\dot{\mathbf{F}}^*) \geqslant 0.$$

The latter is valid to within small quantities which are negligible owing to the hypothesis that $\hat{\mathbf{T}}''$ is a continuous and single valued function of $\mathbf{F}$. From Eqs. (5.8) and (5.9) we obtain

$$(5.10) \qquad \text{tr}[(\mathbf{B}'-\mathbf{B}'')\dot{\mathbf{F}}^*] \geqslant 0;$$

hence, from Eqs. (4.1) and (4.2) we get

$$(5.11) \qquad \text{tr}[(\mathbf{T}'-\mathbf{T}'')\dot{\mathbf{F}}^*\mathbf{F}^{-1}] \geqslant 0.$$

Since the only contravariant component of $\dot{\mathbf{F}}^*\mathbf{F}^{-1}$ which is different from zero is $(\dot{\mathbf{F}}^*\mathbf{F}^{-1})^{ij}$ and since this component is assumed to be positive, we obtain from Eq. (5.11)

$$(5.12) \qquad T'_{ij}-T''_{ij} \geqslant 0, \qquad (T'_{ij} > 0, T''_{ij} > 0).$$

On the other hand, if we suppose that T'_{ij} and T''_{ij} are both negative, the considered increment of deformation $\dot{\mathbf{F}}^*dt$ is an unloading one in view of Definition 2.1 point ii. Hence, by repeating the same reasoning as before and by substituting $-\dot{\mathbf{F}}^*$ to $\dot{\mathbf{F}}^*$, we get

$$(5.13) \qquad -T'_{ij}+T''_{ij} \geqslant 0, \qquad (T'_{ij} < 0, T''_{ij} < 0).$$

From Eqs. (5.12) and (5.13) we deduce

$$(5.14) \qquad |T'_{ij}| \geqslant |T''_{ij}|, \qquad [T'_{ij}T''_{ij} > 0 \,(\text{no sum})].$$

To complete the proof of this theorem, suppose that $T'_{ij} > 0$ and $T''_{ij} > 0$ for a certain value of $\mathbf{F}$, and that, contrary to what is stated by the theorem, $T'_{ij} < T^*_{ij}$. In this case the process from $\mathbf{F}$ to $\mathbf{F}+\dot{\mathbf{F}}^*dt$ is not thermodynamically compatible when the constitutive equations (2.11)–(2.14) hold, as can be easily verified by means of Eqs. (5.8), (5.6) and (4.1). On the other hand, it follows from Eqs. (5.9), (5.6), (5.14) and (4.2) that the process from $\mathbf{F}+\dot{\mathbf{F}}^*dt$ to $\mathbf{F}$ is thermodynamically compatible when Eqs. (2.15)–(2.18) hold. In the latter process, however, the deformation increment is represented by $-\dot{\mathbf{F}}^*$ and, therefore, according to Corollary 4.2, its opposite $\dot{\mathbf{F}}^*$ must represent a loading deformation increment. Thus, we must have $T'_{ij} > T^*_{ij}$. In a similar way we can prove that $T''_{ij} < T^*_{ij}$ when $T'_{ij} > T''_{ij} > 0$, and that $T''_{ij} > T^*_{ij} > T'_{ij}$ when $T'_{ij} < 0$ and $T''_{ij} < 0$.

An immediate consequence of this theorem is the following:

COROLLARY 5.1. Under the hypotheses of Theorem 5.1, if $\mathbf{T}' = \mathbf{T}''$ for a certain value of $\mathbf{F}$ then, for the same value of $\mathbf{F}$, the equalities $\mathbf{T}^* = \mathbf{T}' = \mathbf{T}''$ hold true.

Moreover, it is straightforward matter to argue from Theorem 5.1 and Theorem 5.2 that the functions $\hat{a}$ and $\hat{c}$ which appear in Eqs. (2.19) and (2.21) must be such that

$$(5.15) \qquad \hat{a}(\text{I}, \text{II}, \text{III}, \theta) \geqslant 1 \quad \text{and} \quad \hat{c}(\text{I}, \text{II}, \text{III}, \theta) \geqslant 1.$$

Also, it is immediate to deduce from Theorem 5.2 and from Eq. (5.6) that the function $\hat{b}$ appearing in Eq. (2.20) must be such that

$$(5.16) \qquad 0 < \hat{b}(\text{I}, \text{II}, \text{III},) \geqslant 1.$$

It should be observed, finally, that all the restrictions established in this section for the covariant components of $\mathbf{T}'$, $\mathbf{T}''$ and $\mathbf{T}^*$ hold true also for the mixed or the contravariant components of the same tensors. This is a consequence of the fact that, as previously observed, Corollary 4.1 applies to any kind of components of the tensor $\dot{\mathbf{F}}\mathbf{F}^{-1}$.

6. Determination of free energy and entropy from experimentally measurable quantities

Let us consider an homothermal process ($q \equiv 0$) and let us call $r'_{(\theta)}$ and $r''_{(\theta)}$ the heating supplies which are to be provided to the body during a loading and during an unloading deformation increment, respectively. The index θ appended to the above quantities helps to remind us that they are relevant to the constant temperature θ which is taken into consideration. We shall assume $r'_{(\theta)}$ and $r''_{(\theta)}$ to be positive when they represent an amount of heat which is absorbed by the body in the unit time. By means of the first principle of thermodynamics we can express $r'_{(\theta)}$ and $r''_{(\theta)}$ through F, θ and $\dot{F}$. Indeed, if we consider a loading deformation process from F to $F + \dot{F}dt$ and if we apply the first principle of thermodynamics, we get

$$(6.1) \qquad \varrho\dot{\varepsilon} = \varrho r'_{(\theta)} + \mathrm{tr}(T'\dot{F}F^{-1}).$$

Hence, since in the present case

$$(6.2) \qquad \dot{\varepsilon} = \mathrm{tr}[(\partial_F\hat{\varepsilon})^T\dot{F}],$$

we obtain

$$(6.3) \qquad r'_{(\theta)} = \mathrm{tr}\left\{\left[(\partial_F\hat{\varepsilon})^T - \frac{1}{\varrho}F^{-1}T'\right]\dot{F}\right\}.$$

Thus, if we call H' the second rank tensor given by

$$(6.4) \qquad H' = \hat{H}'(F, \theta) = (\partial_F\hat{\varepsilon})^T - \frac{1}{\varrho}F^{-1}T'$$

we can express $r'_{(\theta)}$ in the form

$$(6.5) \qquad r'_{(\theta)} = \hat{r}'_{(\theta)}(F, \theta, \dot{F}) = \mathrm{tr}(H'\dot{F}).$$

It should be clear that since Eq. (6.5) is valid for any loading deformation increment whatsoever, it allows us to determine $\hat{H}'$ once $\hat{r}'_{(\theta)}$ is known. Thus H' can be determined experimentally from measurements of $r'_{(\theta)}$, even if $\hat{\varepsilon}$ is not known. Similarly, if we consider a process from F to $F - \dot{F}dt$, which is an unloading process since we have assumed that $\dot{F}dt$ is a loading deformation increment, we can obtain

$$(6.6) \qquad r''_{(\theta)} = \cdot + \frac{1}{\varrho}\mathrm{tr}(T''\dot{F}F^{-1}) = -\mathrm{tr}\left\{\left[(\partial_F\hat{\varepsilon})^T - \frac{1}{\varrho}F^{-1}T''\right]\dot{F}\right\}.$$

Hence,

$$(6.7) \qquad r''_{(\theta)} = \hat{r}''_{(\theta)}(F, \theta, -\dot{F}) = -\mathrm{tr}(H''\dot{F}),$$

where H'' is the second rank tensor given by

$$(6.8) \qquad H'' = \hat{H}''(F, \theta) = (\partial_F\hat{\varepsilon})^T - \frac{1}{\varrho}F^{-1}T''.$$

It follows from Eq. (6.7) that H'', analogously to H', can be determined once $\hat{r}''_{(\theta)}$ is known. Equations (6.5) and (6.7) tell us that both $\hat{r}'_{(\theta)}$ and $\hat{r}''_{(\theta)}$ are odd functions of $\dot{F}$. Care must be exercised, however, in noting that $r'_{(\theta)}$ and $r''_{(\theta)}$ are relevant only to loading and to unloading processes, respectively. So that, if $\dot{F}$ represents a loading deformation increment,

it is not possible to measure $r'_{(\theta)}$ for the increment $-\dot{\mathbf{F}}$ or $r''_{(\theta)}$ for the increment $\dot{\mathbf{F}}$ although analytical expressions are meaningful both for $\dot{\mathbf{F}}$ and $-\dot{\mathbf{F}}$. From Eqs. (6.4) and (6.8) we get

$$(6.9) \qquad (\partial_\mathbf{F}\hat{\varepsilon})^T = \frac{1}{\varrho}\mathbf{F}^{-1}\mathbf{T}' + \mathbf{H}' = \frac{1}{\varrho}\mathbf{F}^{-1}\mathbf{T}'' + \mathbf{H}''$$

which shows that one of the four quantities $\mathbf{T}'$, $\mathbf{T}''$, $\mathbf{H}'$ and $\mathbf{H}''$ can be determined once the other three are given.

By means of Eqs. (3.9) and (3.10) we can express $\partial_\mathbf{F}\hat{\varepsilon}$ in the form

$$(6.10) \qquad \partial_\mathbf{F}\hat{\varepsilon} = \partial_\mathbf{F}\hat{\psi} - \theta\partial_\theta\partial_\mathbf{F}\hat{\psi}.$$

From this and from Eq. (6.4) we get

$$(6.11) \qquad \theta\partial_\theta(\partial_\mathbf{F}\hat{\psi})^T - (\partial_\mathbf{F}\hat{\psi})^T + \frac{1}{\varrho}\mathbf{F}^{-1}\mathbf{T}' + \mathbf{H}' = \mathbf{0}$$

or, in component form,

$$(6.12) \qquad \theta\partial_\theta[(\partial_\mathbf{F}\hat{\psi})^T]_{ij} - [(\partial_\mathbf{F}\hat{\psi})^T]_{ij} + \frac{1}{\varrho}F_{il}^{-1}T'_{lj} + H'_{ij} = 0.$$

This linear differential equation of the first order allows us to calculate the unknown function $[(\partial_\mathbf{F}\hat{\psi})^T]_{ij}$ after integration with respect to θ. Since Eq. (6.12) holds for each component of $(\partial^\mathbf{F}\hat{\psi})^T$ and since $\mathbf{T}'$, $\mathbf{T}''$, $r'_{(\theta)}$ and $r''_{(\theta)}$ (and thus $\mathbf{H}'$ and $\mathbf{H}''$) are experimentally measurable quantities, Eqs. (6.12) provide the means to determine $\partial_\mathbf{F}\hat{\psi}$ from experimental data. Once $\partial_\mathbf{F}\hat{\psi}$ is determined in this way, a further integration with respect to $\mathbf{F}$ gives us $\hat{\psi}$, provided that the compatibility conditions for the existence of a unique function $\hat{\psi}$ are met. After having determined $\hat{\psi}$, it is a straightforward matter to determine $\hat{\eta}$, $\hat{\varepsilon}$ and $\hat{\mathbf{T}}^*$ from Eqs. (3.10), (3.9) and (5.6). It should be remarked that the function $\hat{\eta}$ so determined is relevant to states of deformation which can be attained through irreversible processes only and that, moreover, this function can be determined from experimental data. It is assumed, of course, that the entropy of the materials we are dealing with tends to zero as temperature tends to absolute zero. This assumption holds true for materials that can reach a complete thermodynamical equilibrium at low temperatures and it is known as the third law of thermodynamics or the Nernst-Simon theorem [13].

7. A subclass of elastic materials with hysteresis and thermodynamic derivation of the elastic limit

In the previous section we have seen how internal energy and entropy can be calculated through experimentally measurable quantities. Once entropy is known, we can calculate the function

$$(7.1) \qquad r^*_{(\theta)} = \hat{r}^*_{(\theta)}(\mathbf{F}, \theta, \dot{\mathbf{F}}) = \theta\dot{\eta}$$

which can be interpreted as the heating supply which has to be provided during an isothermal process to an imaginary hyperelastic material which has the same free energy and

entropy of the material taken into consideration. If we apply the first principle of thermo-dynamics to an isothermal process of the above hyperelastic material, we get

$$(7.2) \qquad \varrho \dot{\varepsilon} = \varrho r^*_{(\theta)} + \mathrm{tr}(\mathbf{T}^*\dot{\mathbf{F}}\mathbf{F}^{-1}).$$

Similarly to what has been done for $r'_{(\theta)}$ and $r''_{(\theta)}$, we shall express $r^*_{(\theta)}$ in the form

$$(7.3) \qquad r^*_{(\theta)} = \mathrm{tr}(\mathbf{H}^*\dot{\mathbf{F}}),$$

where the second rank tensor $\mathbf{H}^*$ is given by

$$(7.4) \qquad \mathbf{H}^* = (\partial_{\mathbf{F}}\hat{\varepsilon})^T - \frac{1}{\varrho}\mathbf{F}^{-1}\mathbf{T}^* = \theta(\partial_{\mathbf{F}}\eta)^T.$$

We now have all the ingredients to calculate the *internal dissipation d'* during a loading deformation increment $\dot{\mathbf{F}}dt$ in correspondence to given values of $\mathbf{F}$ and θ. This quantity is given clearly by

$$(7.5) \qquad d' = \hat{d}'(\mathbf{F}, \theta, \dot{\mathbf{F}}) = \hat{r}^*(\mathbf{F}, \theta, \dot{\mathbf{F}}) - \hat{r}'(\mathbf{F}, \theta, \dot{\mathbf{F}}),$$

which, remembering Eqs. (6.5) and (7.3), can be also expressed as

$$(7.6) \qquad d' = \mathrm{tr}[(\mathbf{H}^* - \mathbf{H}')\dot{\mathbf{F}}].$$

Analogously, in correspondence to the same values of $\mathbf{F}$ and θ we can consider an unload-ing deformation increment $-\dot{\mathbf{F}}dt$ opposite to the previous one and we can calculate the *internal dissipation d''* during this unloading deformation increment.

We get

$$(7.7) \qquad d'' = \hat{d}''(\mathbf{F}, \theta, \dot{\mathbf{F}}) = \hat{r}^*(\mathbf{F}, \theta, -\dot{\mathbf{F}}) - \hat{r}''(\mathbf{F}, \theta, -\dot{\mathbf{F}}) = -\hat{r}^*(\mathbf{F}, \theta, \dot{\mathbf{F}}) + \hat{r}''(\mathbf{F}, \theta, \dot{\mathbf{F}}),$$

where we have made use of the fact that $\hat{r}^*$ and $\hat{r}''$ are odd functions of $\dot{\mathbf{F}}$. By means of Eqs. (6.7) and (7.3), we can express Eq. (7.7) in the form

$$(7.8) \qquad d'' = \mathrm{tr}[(\mathbf{H}'' - \mathbf{H}^*)\dot{\mathbf{F}}].$$

From Eqs. (7.6) and (7.8) we can deduce that the *total dissipation* $d_T = \hat{d}_T(\mathbf{F}, \theta, \dot{\mathbf{F}})$ during an infinitesimal cycle $\mathbf{F}, \mathbf{F} + \dot{\mathbf{F}}dt, \mathbf{F}$, is given by

$$(7.9) \qquad d_T = d' + d'' = \mathrm{tr}[(\mathbf{H}'' - \mathbf{H}')\dot{\mathbf{F}}].$$

Since $\dot{\mathbf{F}}$ and $-\dot{\mathbf{F}}$ have been assumed to represent a loading and an unloading deforma-tion increment, respectively, it follows from Theorem 5.1 and from Eqs. (6.4), (6.8) and (7.4) that

$$(7.10) \qquad d' = \frac{1}{\varrho}\mathrm{tr}[\mathbf{F}^{-1}(\mathbf{T}' - \mathbf{T}^*)\dot{\mathbf{F}}] \geqslant 0,$$

$$(7.11) \qquad d'' = \frac{1}{\varrho}\mathrm{tr}[\mathbf{F}^{-1}(\mathbf{T}^* - \mathbf{T}'')\dot{\mathbf{F}}] \geqslant 0$$

and, as a consequence,

$$(7.12) \qquad d_T = \frac{1}{\varrho}\mathrm{tr}[\mathbf{F}^{-1}(T' - T'')\dot{\mathbf{F}}] \geqslant 0.$$

For the sake of simplicity attention will be confined to the subclass of materials for which

$$(7.13) \qquad\qquad d' = \hat{\alpha}(\mathbf{F}, \theta)d'',$$

where α is a positive scalar function of $\mathbf{F}$ and θ. In this subclass of materials the ratio between the amount of energy dissipated during a loading deformation increment and the amount of energy dissipated during an unloading deformation increment opposite to the previous one is given by $\alpha = \hat{\alpha}(\mathbf{F}, \theta)$ and, hence, depends only on $\mathbf{F}$ and θ. From Eqs. (7.9) and (7.13) we obtain

$$(7.14) \qquad\qquad d' = \frac{\alpha}{1+\alpha}\, d_T = \frac{\alpha}{1+\alpha}\, \text{tr}[(\mathbf{H}'' - \mathbf{H}')\dot{\mathbf{F}}]$$

and

$$(7.15) \qquad\qquad d'' = \frac{1}{1+\alpha}\, d_T = \frac{1}{1+\alpha}\, \text{tr}[(\mathbf{H}'' - \mathbf{H}')\dot{\mathbf{F}}].$$

We can now prove the following:

THEOREM 7.1. *In a material in which Eq. (7.13) holds, the quantities* ψ, $\mathbf{T}'$, $\mathbf{T}''$, $\mathbf{H}'$ *and* $\mathbf{H}''$ *are connected by the relation*[10]

$$(7.16) \qquad\qquad \varrho(\partial_{\mathbf{F}}\hat{\psi})^T = \mathbf{F}^{-1}\frac{\mathbf{T}'+\mathbf{T}''}{2} + \varrho\,\frac{\alpha-1}{\alpha+1}\,\frac{\mathbf{H}''-\mathbf{H}'}{2}.$$

P r o o f. From Eqs. (7.10) and (7.11) we obtain

$$(7.17) \qquad\qquad d''-d' = \frac{1}{\varrho}\,\text{tr}[\mathbf{F}^{-1}(2\mathbf{T}^* - \mathbf{T}' - \mathbf{T}'')\dot{\mathbf{F}}],$$

which by means of Eqs. (7.14) and (7.15) can be expressed as

$$(7.18) \qquad\qquad \varrho\,\frac{\alpha-1}{\alpha+1}\,\text{tr}[(\mathbf{H}'' - \mathbf{H}')\dot{\mathbf{F}}] = \text{tr}[\mathbf{F}^{-1}(2\mathbf{T}^* - \mathbf{T}' - \mathbf{T}'')\dot{\mathbf{F}}].$$

Since $\dot{\mathbf{F}}$ is is an arbitrary loading deformation increment, we can deduce from Eq. (7.18) that

$$(7.19) \qquad\qquad 2\mathbf{T}^* - \mathbf{T}' - \mathbf{T}'' = \varrho\,\frac{\alpha-1}{\alpha+1}\,\mathbf{F}(\mathbf{H}'' - \mathbf{H}').$$

From this and from Eq. (5.6) we obtain Eq. (7.16).

Consider an element of material for which Eq. (7.13) holds and suppose that this element undergoes an isothermal deformation process at temperature θ. We shall indicate $\{\bar{\mathbf{F}}\}_\theta$ the set of all the states of deformation $\bar{\mathbf{F}}$ which represent the limit after which the behaviour of the material is no more represented by Eqs. (2.11)–(2.18) owing to the occurrence of phenomena such as failure, plastic yielding and so on. We shall call $\{\mathbf{F}^*\}_\theta$ the set of states of deformation for which $\mathbf{T}' = \mathbf{T}^*$. The following theorem gives us sufficient conditions in order that $\{\bar{\mathbf{F}}\}_\theta \equiv \{\mathbf{F}^*\}_\theta$.

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[10] This formula generalises the well-known one $\mathbf{T} = \varrho\mathbf{F}(\partial_{\mathbf{F}}\hat{\psi})^T$ of the standard approach.

Theorem 7.2. *If the transition from the response described by Eqs.* (2.11)–(2.18) *to another kind of response occurs in such a way that*:

(i) *in correspondence to each value of* $\overline{F}$, *every change in the stress tensor produces a change in the deformation gradient of the body*;

(ii) $\alpha \neq 0$ *in the open interval*[11] $(0, F^*)$;

(iii) *at the points* F^* *the (hyper-)tangent to* $\hat{T}^*$ *is different from that to* $\hat{T}'$ *at the same point*;

then $\{\overline{F}\}_\theta \equiv \{F^*\}_\theta$.

Proof. From (i) and (ii) it follows that $\overline{F}$ cannot be contained in the interval $(0, F^*)$. To prove this, observe that (i) requires that $T'(\overline{F}) = T''(\overline{F})$ and that, since $\alpha \neq 0$ in $(0, F^*)$, T' and T'' cannot coincide for $F \in (0, F^*)$ as it follows from Eqs. (7.13), (7.10) and (7.11) and from the fact that $T' \neq T^*$. Thus $\overline{F} \notin (0, F^*)$. On the other hand we can deduce from [iii] that the curve T^* intersects the curve $\hat{T}'$ at the point F^*. Therefore, from a Lemma proved in [11, § 6] we can infer that the material cannot reach a state of deformation outside the interval $(0, F^*)$ when its constitutive equations are given by Eqs. (2.11)–(2.18). Hence $\{\overline{F}\}_\theta \equiv \{F^*\}_\theta$.

Acknowledgement

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[11] By open interval $(0, F^*)$ we mean the set of tensors F such as $0 < F_{IJ} < F_{IJ}^*$.

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